

**CLAIMS**

1. Method of manufacturing a metal oxide, metal oxidhydroxide or metal hydroxide product, said product having a sub-micron primary particle size, comprising the steps of:
- 5 - Introducing a solid reactor filling material in a reactor,  
- introducing a metal-containing precursor in said reactor,  
- introducing a co-solvent into the said reactor,  
- introducing a supercritical solvent into the said reactor, thereby  
- establishing a contact between the metal-containing precursor and the co-solvent, thus  
10 - resulting in the formation of said product in the proximity of the said solid reactor filling material.
2. Method according to claim 1, wherein the formation of said product takes place by a process involving at least a sol-gel reaction.
- 15 3. Method according to claim 1 or claim 2, wherein the metal oxide, metal oxidhydroxide or metal hydroxide product is substantially crystalline.
4. Method according to claim 1 or claim 2, wherein the metal oxide, metal oxidhydroxide  
20 or metal hydroxide product is substantially amorphous.
5. Method according to claim 1 or claim 2, wherein the metal oxide, metal oxidhydroxide or metal hydroxide product is a mixture of several different phases.
- 25 6. Method according to any of claims 1-5, wherein the introduction of the solid reactor filling material, the metal-containing precursor, the co-solvent, and the supercritical solvent into the said reactor is done in arbitrary order.
7. Method according to any of claims 1-6, wherein at least one of the solid reactor filling  
30 material, the metal-containing precursor, the co-solvent or the supercritical solvent is mixed with at least one of the solid reactor filling material, the metal-containing precursor, the co-solvent or the supercritical solvent before introduction into the said reactor.
8. Method according to any of claims 1-7, wherein the metal oxide, metal oxidhydroxide or  
35 metal hydroxide product is manufactured in a mode selected from the group of: a batch mode, a quasi-batch mode and a substantially continuous mode.

9. Method according to any of claims 1-8, wherein a temperature in the reactor during the formation of said product is kept at a fixed temperature.
10. Method according to any of claims 1-8, wherein a temperature in the reactor during  
5 the formation of said product is performed at an increasing temperature.
11. Method according to any of claims 1-8, wherein a temperature in the reactor during the formation of said product is performed at a decreasing temperature.
- 10 12. Method according to any of claims 1-8, wherein a temperature in the reactor during the formation of said product is performed at a temperature profile being an arbitrary combination at least two of the temperature profiles: a fixed temperature, a decreasing temperature, a decreasing temperature.
- 15 13. Method according to any of claims 9-12, wherein the temperature in the reactor during the formation of said product is maximum 400°C, more preferably maximum 300°C, even more preferably maximum 200°C, most preferably maximum 100°C, and even and most preferably maximum 50°C.
- 20 14. Method according to any of claims 1-13, wherein a pressure in the reactor during the formation of said product is kept at a fixed pressure.
15. Method according to any of claims 1-13, wherein a pressure in the reactor during the formation of said product is performed at an increasing pressure.
- 25 16. Method according to any of claima 1-13, wherein a pressure in the reactor during the formation of said product is performed at a decreasing pressure.
17. Method according to any of claims 1-8, wherein a pressure in the reactor during the  
30 formation of said product is performed at a pressure profile being an arbitrary combination at least two of the pressure profiles: a fixed pressure, a decreasing pressure, a decreasing pressure.
18. Method according to any of claims 1-17, wherein the supercritical solvent is CO<sub>2</sub>, and  
35 wherein the pressure in the reactor during the formation of said product is minimum 74 bar, more alternatively minimum 80 bar, even more alternatively minimum 90 bar, and most alternatively minimum 100 bar.

19. Method according to any of claims 1-18, wherein the supercritical solvent is CO<sub>2</sub>, and wherein the temperature in the reactor during the formation of said product is minimum 31°C, alternatively 43°C, more alternatively minimum 100°C, even more alternatively minimum 200°C, most alternatively minimum 300°C, and even and most alternatively  
5 minimum 400°C.
20. Method according to any of claims 1-17, wherein the supercritical solvent is isopropanol, and wherein the pressure in the reactor during the formation of said product is minimum 47 bar, more alternatively minimum 80 bar, even more alternatively minimum  
10 90 bar, and most alternatively minimum 100 bar.
21. Method according to any of claims 1-17 or claim 20, wherein the supercritical solvent is isopropanol, and wherein the temperature in the reactor during the formation of said product is minimum 235°C, more alternatively minimum 250°C, even more alternatively  
15 minimum 270°C, most alternatively minimum 300°C, and even and most alternatively minimum 400°C.
22. Method according to any of claims 1-21, wherein the supercritical solvent is supercritical before the introduction into said reactor.  
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23. Method according to any of claims 1-21, wherein the supercritical solvent is brought into a supercritical phase after the introduction into said reactor.
24. Method according to any of claims 1-23, wherein the time of the formation of said  
25 product is maximum 1 hour, preferably maximum 0,75 hour, and most preferably maximum 0,5 hour.
25. Method according to any of claims 1-24, wherein the time of the formation of said product is maximum 8 hours, preferably maximum 6 hours, and most preferably maximum  
30 2 hours.
26. Method according to any of claims 1-25, wherein the time of the formation of said product is maximum 24 hours, preferably maximum 17 hours, and most preferably maximum 10 hours.  
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27. Method according to any of claims 1-26, wherein a plurality of different metal-containing precursors is introduced in said reactor.

28. Method according to any of claims 1-27, wherein the metal-containing precursor is a metal alkoxide.
29. Method according to any of claims 1-28, wherein the metal-containing precursor is  
5 selected from the group of : titanium tetraisopropoxide, titanium butoxide, titanium ethoxide, and titanium methoxide.
30. Method according to any of claims 1-28, wherein the metal-containing precursor is selected from the group of: aluminium isopropoxide and aluminium-sec-butoxide.
- 10 31. Method according to claim 1, wherein the metal-containing precursor is magnesium ethoxide.
32. Method according to any of claims 1-27, wherein the metal-containing precursor is a  
15 metal salt.
33. Method according to any of claims 1-27 or claim 32, wherein the metal-containing precursor is  $\text{Ti}(\text{SO}_4)_2$ .
- 20 34. Method according to any of claims 1-27 or claim 32, wherein the metal-containing precursor is selected from the group of:  $\text{TiCl}_4$  and  $\text{AlCl}_3$ .
35. Method according to any of claims 1-34, wherein the co-solvent is selected from the group of: water, ethanol, methanol, hydrogenperoxid and isopropanol.
- 25 36. Method according to any of claims 1-34, wherein a plurality of different co-solvents is introduced in said reactor.
37. Method according to any of claims 1-36, wherein the solid reactor filling material  
30 functions as a heterogeneous catalyst.
38. Method according to claim 37, wherein the solid reactor filling material comprises at least one promoter.
- 35 39. Method according to any of claims 1-38, wherein the solid reactor filling material is constituted by at least one fibre.
40. Method according to any of claims 1-38, wherein the solid reactor filling material is constituted by a powder.

41. Method according to any of claims 1-38, wherein the solid reactor filling material has the shape selected from the group of: a sponge, a grid, a wad of fibres, and a sheet.
42. Method according to any of claims 1-41, wherein the solid reactor filling material has a substantially porous structure.
43. Method according to any of claims 1-42, wherein the solid reactor filling material has a size and shape capable of substantially confining the metal-containing precursor to a limited part of the reactor.
44. Method according to any of claims 1-43, wherein the solid reactor filling material comprises a polymer.
45. Method according to claim 44, wherein the polymer is selected from the group of: polystyrene (PS), polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), and polyvinyl acetate (PVAc).
46. Method according to claim 44, wherein the polymer is selected from the group of: acrylic polymer, fluorinated polymer, diene polymer, vinyl copolymer, polyamide polymer, polyester polymer, polyether polymer, and polyimide polymer.
47. Method according to any of claims 1-46, wherein the solid reactor filling material comprises a metal.
48. Method according to claim 47, wherein the metal is selected from the group of: titanium, aluminium, zinc, vanadium, magnesium, zirconium, chromium, molybdenum, niobium, tungsten, copper, and iron.
49. Method according to any of claims 1-48, wherein the solid reactor filling material comprises a metal oxide.
50. Method according to claim 49, wherein the metal oxide is selected from the group of: titanium oxide, zinc oxide, copper oxide, aluminium oxide, vanadium oxide, magnesium oxide, zirconium oxide, chromium oxide, silicon oxide, molybdenum oxide, niobium oxide, tungsten oxide, and iron oxide.
51. Method according to any of claims 1-50, wherein the solid reactor filling material comprises a ceramic.

52. Method according to any of claims 1-51, wherein the solid reactor filling material comprises a metal sulphate.
53. Method according to any of claims 1-52, wherein the solid reactor filling material  
5 comprises a metal halide.
54. Method according to any of claims 1-53, wherein the solid reactor filling material comprises a metal oxide, a metal oxidhydroxide or a metal hydroxide identical to said product resulting from the formation in said reactor.
- 10 55. Method according to any of claims 1-53, wherein the solid reactor filling material functions as seed material for the formation of said product.
56. Method according to any of claims 1-54, wherein the solid reactor filling material  
15 functions as a collecting agent for the said product.
57. Method according to any of claims 1-56, wherein said product is separable from the solid reactor filling material with no further treatments of the solid reactor filling material.
- 20 58. Method according to any of claims 1-57, wherein said product is separable from the solid reactor filling material without substantially degrading the solid reactor filling material.
59. Method according to any if claims 1-58, wherein said product is separable from the  
25 solid reactor filling material in a way that allows the solid reactor filling material to be re-used as solid reactor filling material.
60. Method according to any of claims 1-59, wherein said product is separable from the solid reactor filling material by flushing the solid reactor filling material in a fluid.
- 30 61. Method according to any of claims 1-60, wherein said product is separable from the solid reactor filling material by vacuum means.
62. Method according to any of claims 1-61, wherein said product is separable from the  
35 solid reactor filling material by blowing means.
63. Method according to any of claims 1-62, wherein said product is separable from the solid reactor filling material by ultrasonic means.

64. Metal oxide, metal oxidhydroxide or metal hydroxide product being manufactured by the method according to any of claims 1-63, wherein the metal oxide, metal oxidhydroxide or metal hydroxide product is in the form of aggregates of primary particles with an average primary particle size of maximum 1000 nm, preferably maximum 500 nm, and most preferably maximum 100 nm.
65. Metal oxide product being manufactured by the method according to any of claims 1-63, wherein the metal oxide, metal oxidhydroxide or metal hydroxide product is in the form of aggregates of primary particles with an average primary particle size of 100 nm, preferably maximum 50 nm, more preferably maximum 20 nm, and most preferably maximum 10 nm.
66. Metal oxide product being manufactured by the method according to any of claims 1-63, wherein the metal oxide product is  $\text{TiO}_2$ , preferably with a crystallinity of minimum 20%, preferably minimum 30%, more preferably minimum 40%, and even more preferably minimum 60% and even most preferably minimum 80%.
67. Metal oxide product being manufactured by the method according to any of claims 1-63, wherein the metal oxide product is  $\text{TiO}_2$  of anatase structure.
68. Metal oxide product being manufactured by the method according to any of claimd 1-63, wherein the metal oxide is from the group of:  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{WO}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{TaO}_3$ ,  $\text{CuO}$ ,  $\text{CoO}$ ,  $\text{NiO}$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{ZnO}$ .
69. Metal oxidhydroxide product being manufactured by the method according to any of claims 1-63, wherein the metal oxidhydroxide is from the group of: iron oxidhydroxide, titanium oxidehydroxide, manganese oxidhydroxide and aluminium oxidhydroxide.
70. Metal oxidhydroxide product being manufactured by the method according to any of claims 1-63, wherein the metal oxidhydroxide is aluminium oxidhydroxide of Boehmite structure.
71. Metal hydroxide product being manufactured by the method according to any of claims 1-63, wherein the metal hydroxide is from the group of: iron hydroxide, silicium hydroxide, zirconium hydroxide, titanium hydroxide, manganese hydroxide and aluminium hydroxide.

72. Apparatus for manufacturing a metal oxide, metal oxidhydroxide or metal hydroxide product, said product having a sub-micron primary particle size, comprising the following components:

- means for introducing a solid reactor filling material in a reactor,
- 5 - means for introducing a metal-containing precursor in said reactor,
- means for introducing a co-solvent into the said reactor,
- means for introducing a supercritical solvent into the said reactor,
- said reactor intended as a space for establishing a contact between the metal-containing precursor and the co-solvent and
- 10 - said reactor intended as a space for the formation of said product in the proximity of the said solid reactor filling material.